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Determination of vapour pressure and henry's constant of deltamethrin technical using gas saturation method with HPLC detection

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ABSTRACT

The vapour pressure of deltamethrin technical was conducted using the gas saturation method based on the regulatory OPPTS 830.7950 and EEC A.4 guidelines. According to this method the packed vapour saturator columns were connected to vapour pressure apparatus and the columns were exposed to different flow rates. The flow rates were 20 (F1), 40(F2) and 60 mL/min (F3). This set up was equilibrated at 30°C over night. After equilibration the nitrogen gas outlet from the column was connected to the trapping system. Nitrogen gas was continuously passed through each saturator column for 7 days. The maintained flow rate and temperatures were monitored during the study period. At the end of 7 days, the trapping material was collected from the trapping tube by eluting the glass columns using 100 mL of acetone. The collected elute was concentrated using rotary vacuum evaporator to near dryness, and diluted to 10 mL by using acetonitrile. The samples were analysed using validated HPLC. The vapour pressure of deltamethrin technical, was determined to be 1.63×10^{-5} Pa at 20°C and 2.05×10^{-5} Pa at 30°C and the henry's law constant of the test item, deltamethrin technical, was determined to be 2.967×10^3 at 20°C and 2.517×10^3 at 30°C.

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KEYWORDS

Deltamethrin;
 Gas saturation method;
 HPLC;
 Vapour pressure;
 Henry's constant.

INTRODUCTION

The vapor pressure of solid & liquid compounds can be helpful to decide the thermodynamics stability and time span of usability of an assortment of items, particularly those from the pharmaceutical business^[1-3]. The precise capability of vapor pressure can be vital for the sheltered utilize and treatment of strong mixes^[4-7]. Vapor pressure (VP) is an imperative component for the investigation of the natural destiny, transport and appropriation of the mixes in water, air and soil^[8]. For

natural toxins, their VP decides their circulation between the environment and the soil. The vapor pressure of harmful chemicals can be utilized to assess the rate of evaporation after a spill^[9-11]. Vapor pressure information is additionally utilized as a part of the estimation of viscosity, enthalpy of vaporization, air-water segment coefficient, and some other critical Physico-Chemical properties of the mixes.

Deltamethrin items are among the most prevalent and broadly utilized bug sprays as a part of the world and have turned out to be extremely prominent with

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vermin control administrators and people in the United States. This material is an individual from one of the most secure classes of pesticides: Synthetic Pyrethroids^[12]. This pesticide is exceptionally poisonous to aquatic lifestyles, specifically fish, and therefore should be used with excessive caution around water. Although generally taken into consideration secure to use around human beings, it's far nonetheless neurotoxic to humans. deltamethrin is able to pass from a lady's pores and skin via her blood and into her breast milk. there are numerous uses for deltamethrin, ranging from agricultural uses to domestic pest manage. deltamethrin has been instrumental in stopping the spread of diseases carried with the aid of tick-infested prairie dogs, rodents and other borrowing animals. it's miles beneficial in getting rid of and stopping a huge variety of household pests, in particular spiders, fleas, ticks, chippie ants, carpenter bees, cockroaches and bed insects.

EXPERIMENTAL

Materials and methods

The analytical standard of deltamethrin (99.6%) and the sample of deltamethrin (98.9%) were obtained from Sigma Aldrich. The HPLC grade solvents i.e., acetonitrile, water and acetone from Rankem, New Delhi. The analytical reagent grade of sulphuric acid purchased from Merck India Pvt Ltd and Reagent water used in this study was demineralized and purified using a Millipore Milli-Q Purification Water System. Sea sand sourced from Visakhapatnam, India, sea sand was used as solid support for the test item within the saturator columns. The sea sand was sieved to get uniform size particles. The sand was washed prior to use with sulphuric acid, Milli-Q® water followed by acetone and dried at approximately 120°C. Nitrogen gas (Purity 99.999%) supplied by BOC India Ltd., Mumbai, India, was used as carrier gas in this study.

Silica gel of mesh size 60 to 120 supplied by Merck limited, Mumbai, India was used as a trapping agent to collect Permethrin technical vapour. A digital temperature controlled vapour pressure apparatus, supplied by Labindia Instruments Private Limited, Chennai, India, was used in this study. The carrier gas flow rate was measured using manual flow meter supplied by Shimadzu Corporation, Japan. Stainless steel columns of 60 cm

× 15 mm dimensions fitted with adapters at both ends were used in this study. The trapping material (10–11 g of silica gel) was packed in flexible polypropylene tubes having both ends plugged with cotton swabs. The outlet of the stainless steel saturator column was connected to the polypropylene tubes filled with silica gel. To measure the gas flow, a manual flow meter was connected at the trap end. Buchi rotavapour temperature controlled vacuum rotary evaporator - M/s. Buchi Labortechnik, AG, Switzerland was used in this study. A hot air oven supplied by Scientific Systems, Chennai, India was used in this study.

Chromatographic separation parameters

The HPLC-UV framework utilized, comprised shimadzu high performance liquid chromatography with LC-20AT pump and SPD-20A interfaced with LC solution software, furnished with a reversed phase C18 analytical column of 250 mm x 4.6 mm and particle size 5 µm (Phenomenex Luna-C18) Column temperature was kept up at 30°C. The injected sample volume was 10µL. Mobile Phases A and B was Acetonitrile and HPLC Water (90: 10 (v/v)). The flow- rate used was kept at 1.0 mL/min. A detector wavelength was 225 nm. The retention time of deltamethrin about 4.2 min.

Method validation

The method for the determination of deltamethrin technical was validated in terms of method specificity, linearity, assay accuracy and precision.

Specificity

The specificity of the method was checked by HPLC analysis with aliquots of distilled water, acetonitrile and respective standard and test item of deltamethrin technical.

Linearity

Stock solution preparation 0.00531 g [5.31mg] of Deltamethrin PESTANAL® (99.6%) was weighed accurately into a clean and dry 20mL volumetric flask and dissolved with acetonitrile (HPLC grade) and made upto the mark with same. A linear curve was plotted for the concentration of standard versus observed peak area and the correlation coefficient was determined. Lower concentrations were prepared by making appropriate dilutions as mentioned in the below table.

Concentration of solution taken for dilution ($\mu\text{g/ml}$)	Dilution details		Concentration of diluted solution ($\mu\text{g/ml}$)
	Volume taken (mL)	Volume made up to (mL)	
264	3.788	10	100
100	5.000	10	50
50	2.000	10	10
10	1.000	10	1
1	1.000	10	0.1
0.1	1.000	10	0.01

Recovery from trapping agent (silica gel)

The recovery test was performed in order to validate the analytical method for Deltamethrin Technical analysis. Approximately 10 g of silica gel was weighed and this was fortified with Deltamethrin Standard Concentrate at 0.01 $\mu\text{g/ml}$ (T1), 0.10 $\mu\text{g/ml}$ (T2) concentration levels. Each concentration was fortified for 5 times and they were coded as S1 (S1R1 ... S1R5), S2 (S2R1...S2R5). The replicates were transferred to glass chromatographic column and extracted with 100 mL acetone. The extract from each column was concentrated to near dryness and made upto 10 mL with acetonitrile. Two control samples were maintained (S0R1 and S0R2) using unfortified Silica gel.

Preliminary test

Preparation of fine sand as an inert support

Sand was sieved with 0.2 mm sieve to get fine sand with uniform particles. Then the sand was washed with concentrated sulfuric acid for 24 hrs followed by washing with distilled water and acetone and dried at 105°C for an hour. After drying, the sand was allowed to attain room temperature and then used for analysis.

Preparation of the saturator columns

Accurately 6.0 g of Deltamethrin Technical was weighed into a 100 ml beaker, and dissolved with 50 ml of Acetone, and thoroughly mixed with 360 g of fine sand. The treated sand was thoroughly mixed and air dried for half an hour to evaporate acetone. The saturator columns were prepared by weighing and packing 60 g of treated fine sand into each of three stainless steel columns. The columns were coded C1, C2 and C3. The remaining test item coated sand was packed in three separate Glass containers with 60g of

sand and kept in the oven at 30°C for stability analysis after preliminary test.

Flow rate selection

The packed vapour saturator columns were connected to vapour pressure apparatus and the columns were exposed to different flow rates. The flow rates were 20 (F1), 40(F2) and 60 mL/min (F3). This set up was equilibrated at 30°C over night. After equilibration the nitrogen gas outlet from the column was connected to the trapping system. Nitrogen gas was continuously passed through each saturator column for 7 days. The maintained flow rate and temperatures were monitored during the study period. At the end of 7 days, the trapping material was collected from the trapping tube by eluting the glass columns using 100 mL of acetone. The collected elute was concentrated using rotary vacuum evaporator to near dryness, and diluted to 10 mL by using acetonitrile. The samples were analysed using

Stability confirmation

The 60 g coated sand from Day 0 and from glass containers after 7 days of incubation in oven was extracted in duplicate and eluted with 100 mL acetone in glass columns. The elute was collected in 100 ml volumetric flask and made upto the mark with acetonitrile. From that solution 0.1 mL was pipette out and transferred into a 20 mL volumetric flask and made upto the mark using acetonitrile. The samples were then analysed using HPLC.

Definitive test

Accurately 6.03 g of Deltamethrin Technical was weighed into 100 ml beaker, and it was dissolved with 50 ml of acetone, and thoroughly mixed with 360g of fine sand in a glass bowl The treated fine sand was thoroughly mixed and air dried to evaporate acetone. The stainless steel saturated columns were then filled with deltamethrin Technical coated sand. The columns were coded as Te1R1, Te1R2, Te1R3 were set to equilibrate at 30°C. Te2R1, Te2R2, Te2R3 were set to equilibrate at 20°C. The system was allowed to equilibrate overnight. After equilibration the column inlets were connected to nitrogen flow of 40 mL/min. The second end of the saturator column was connected to the trapping tube.

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The experiment was continued for 7 days. The column chamber temperature and flow rate was monitored twice per day. The remaining treated fine sand was stored in glass container and kept in oven of vapour pressure at 20°C for stability analysis during the definitive test.

After 7 days, the trapping material (silica gel) was collected from the trapping tube. The trapping material was transferred to glass columns and the test item was eluted using 100 mL of acetone. The collected elute was concentrated using rotary vacuum evaporator to near dryness, and diluted to 5 mL using acetonitrile and directly injected by HPLC.

Calculations

Recovery

$$\text{Recovered Concentration} = \frac{\text{Sample Area} - \text{Intercept} \times \text{Dilution factor}}{\text{Slope}}$$

$$\text{Mass of Test Item Collected in g} = \frac{\text{Recovered concentration} \times \text{Extract volume}}{10^6}$$

Vapour pressure

The vapour pressure of the test item was calculated using the following equation:

$$p = W/V \times RT/M$$

Where:

p = Vapour pressure (Pa)

W = Mass of the test item collected (g)

V = Volume of gas (m³) [flow-rate (m³/min) × exposure time (min)]

R = Universal molar gas constant 8.314 (J mol⁻¹ K⁻¹)

T = Temperature (K)

M = Molar mass of the test substance (505.2 g/mole)

Henry's constant

At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

$$\text{Formula} = \text{Henry's constant} = C_{\text{water}} / C_{\text{air}} = S \times T \times 82.08 \times 760 / P \times \text{GMW} \times 10^6$$

Where:

C_{water} = Conc. of Deltamethrin in water (in microgram/ml)

C_{air} = Conc. of Deltamethrin in air (in microgram/ml)

ml)

S = Solubility of Deltamethrin (in microgram/ml)

T = Absolute temp (in Kelvin = °C + 273.15)

82.08 = Gas constant, R, [(ml x atm) / (K x mol)]

760 = mm/atm

P = Vapour pressure (in Torr) of Deltamethrin

GMW = gram molecular weight of Deltamethrin (in g/mol) (505.2 g/mol)

To convert vapour pressure Pa to Torr (1 Pa = 1/1.333 x 10² Torr).

RESULTS AND DISCUSSION

Method validation

Linearity of response

A plot of the found peak area of Deltamethrin PESTANAL[®] standard and the concentration of Deltamethrin PESTANAL[®] standard in the samples showed acceptable linearity, as indicated by the correlation coefficient of 0.9999. The data are presented in TABLE 1. A representative calibration curve is

TABLE 1 : Linearity of deltamethrin Standard

Concentration (µg/mL)	Observed Area (mAu)
0.01	362
0.1	3359
1	35486
10	323923
50	1501874
100	3097384
Correlation Coefficient	0.9999
Slope	30799
Intercept	63.60

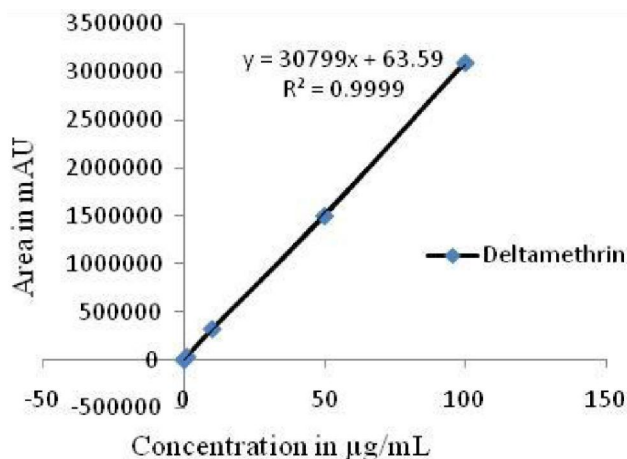
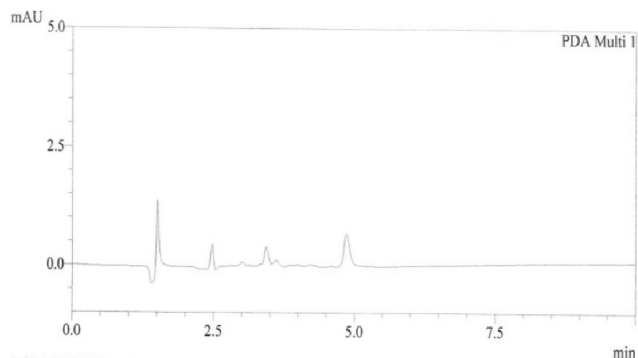


Figure 1 : Calibration curve of deltamethrin



1 PDA Multi 1/225nm 4nm
Figure 2 : Representative chromatogram of silica-gel control

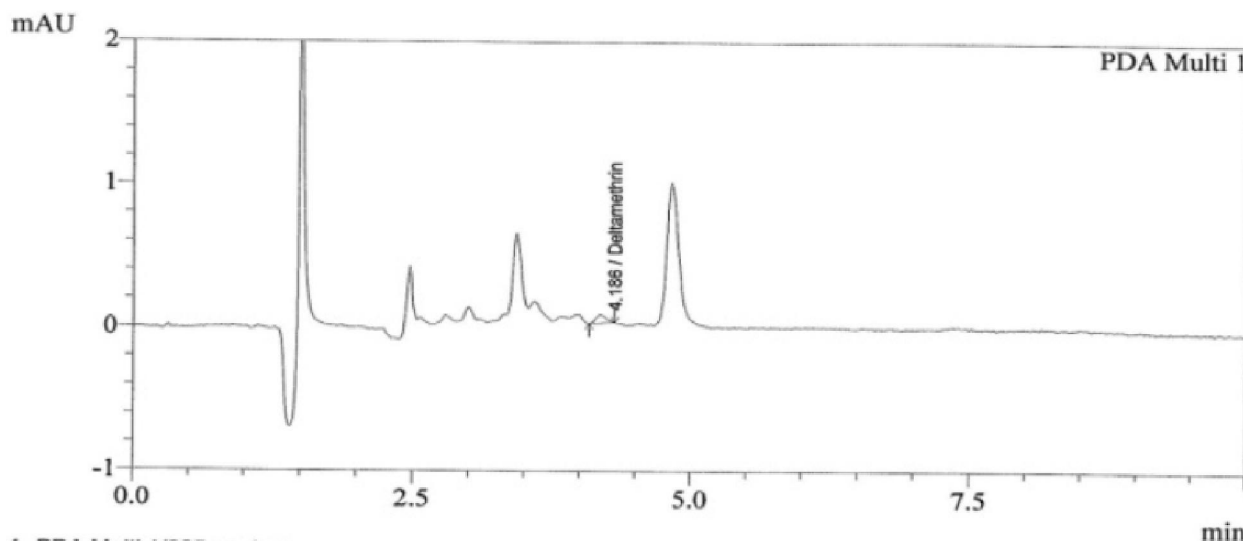
presented in Figure 1.

Specificity

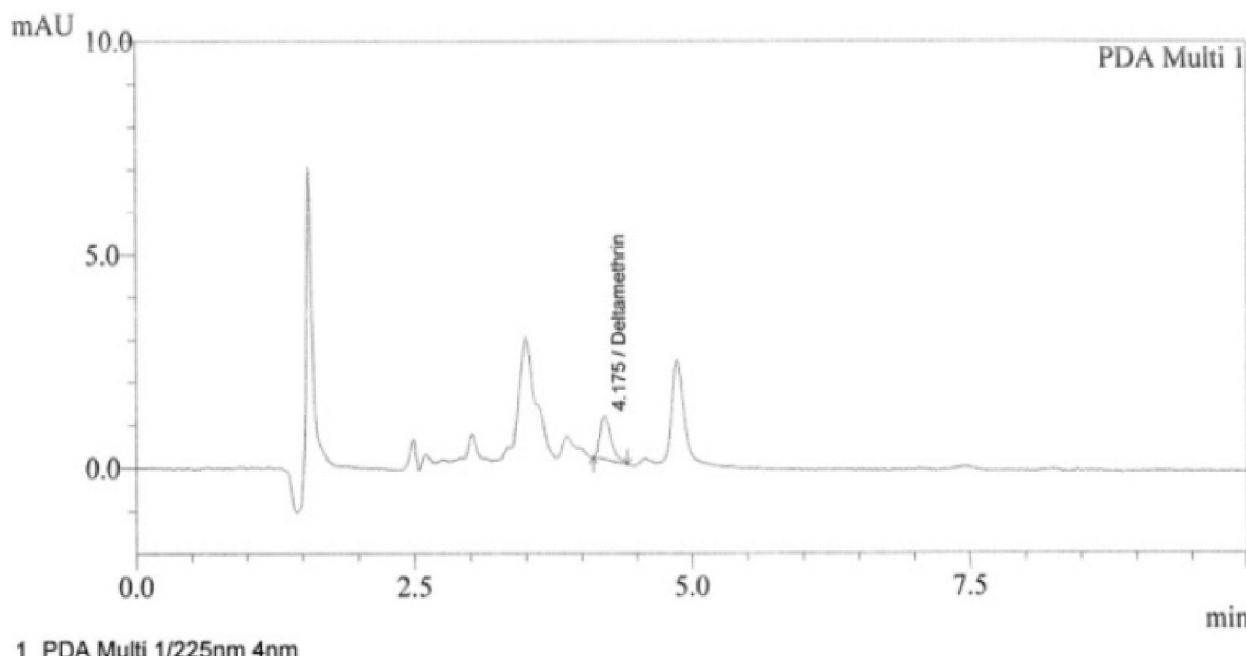
No significant interference was observed from acetonitrile used in the extraction of silica gel.

Recovery from trapping agent (silica gel)

Recovery studies conducted with the trapping agent at two concentrations 0.01 ppm and 0.10 ppm showed an acceptable recovery of 99.36 and 99.12%, respectively. The percentage relative standard deviation (RSD) was 0.44 and 0.12 for the 0.01 $\mu\text{g/ml}$ and 0.10



1 PDA Multi 1/225nm 4nm
Figure 3 : Representative chromatogram of deltamethrin pure from the trapping system recovery experiment (0.01 mg/l)



1 PDA Multi 1/225nm 4nm
Figure 4 : Representative chromatogram of deltamethrin pure from the trapping system recovery experiment (0.1 mg/l)

TABLE 2: Recovery of deltamethrin technical from trapping agent (silica gel): method validation

Sample Code	Area	Slope Obtained from the calibration curve	Intercept Obtained from the calibration curve	Fortified Concentration of Deltamethrin Pure ($\mu\text{g/ml}$)	Total recovered of Deltamethrin Pure ($\mu\text{g/ml}$)	Recovery (%)	Average Recovery (%)	Relative standard deviation (%)
Standard	35476	30798.87	63.60	NF	NF	--		
S0R1	BDL	30798.87	63.60	NF	NF	--	NF	NF
S0R2	BDL	30798.87	63.60	NF	NF	--		
S1R1	368	30798.87	63.60	0.01	0.0099	98.84		
S1R2	371	30798.87	63.60	0.01	0.0100	99.81		
S1R3	369	30798.87	63.60	0.01	0.0099	99.16	99.36	0.44
S1R4	371	30798.87	63.60	0.01	0.0100	99.81		
S1R5	369	30798.87	63.60	0.01	0.0099	99.16		
S2R1	3115	30798.87	63.60	0.10	0.0991	99.08		
S2R2	3120	30798.87	63.60	0.10	0.0992	99.24		
S2R3	3111	30798.87	63.60	0.10	0.0989	98.95	99.12	0.12
S2R4	3120	30798.87	63.60	0.10	0.0992	99.24		
S2R5	3116	30798.87	63.60	0.10	0.0991	99.11		

Key: NF – Not Fortified.; BDL – Below Detection Limit

$\mu\text{g/ml}$ samples, respectively. The results are presented in TABLE 2. Representative chromatograms presented in Figure 2, 3 and Figure 4.

Preliminary test

The preliminary test was conducted at 30°C with three different carrier gas flow rates.

The results are summarized in the following table:

Sample Code	Temperature ($^\circ\text{C}$)	Carrier flow rate Gas * Flow rate (mL/min)	Volume carrier gas (m^3)	Amount trapped (mg)	concentration (mg/m^3)
F2		20	0.2016	0.001	0.00285
F3	30	40	0.4032	0.002	0.00404
F4		60	0.6048	0.002	0.00401

*Average flow rate calculated for 7 days

period at 30°C . The average recovery of triplicate analysis of 60 g samples after 7 days of storage was 99.82% at 30°C and 99.67% at 20°C respectively.

Definitive test

In the definitive experiment, three replicate sand samples coated with Deltamethrin Pure were tested at two different temperatures (20 and 30°C) for a period of 7 days, using a carrier gas flow rate of approximately 40 mL/min . TABLE 4 presents the temperature and flow rate data analysis of the sorbent traps maintained at 20°C experiment showed vapour pressure for the

Based on the above results, a nitrogen flow rate of approximately 40 mL/min was selected for definitive test. The carrier gas was in saturation equilibrium with Deltamethrin Pure at this flow-rate.

Stability confirmation

The results presented in TABLE 3 clearly show that Deltamethrin Pure was stable during the 7 day storage

average mass of Deltamethrin Pure collected after 7 days as $2.05 \times 10^{-5} \text{ g}$. Analysis of the sorbent traps maintained at 30°C experiment showed vapour pressure for the mass of Deltamethrin Pure collected after 7 days as 1.63×10^{-5} . Representative chromatograms from the analysis of the sorbent traps at 30°C and 20°C experiments are presented in Figure 5 and Figure 6 respectively.

Using the mass of the Deltamethrin Pure collected during the experiment and the total volume of gas used, the vapour pressure of the Deltamethrin Pure at 30°C and 20°C was calculated. The results are presented in

TABLE 3 : Stability of deltamethrin technical from the coated sand samples preliminary study – 7th day

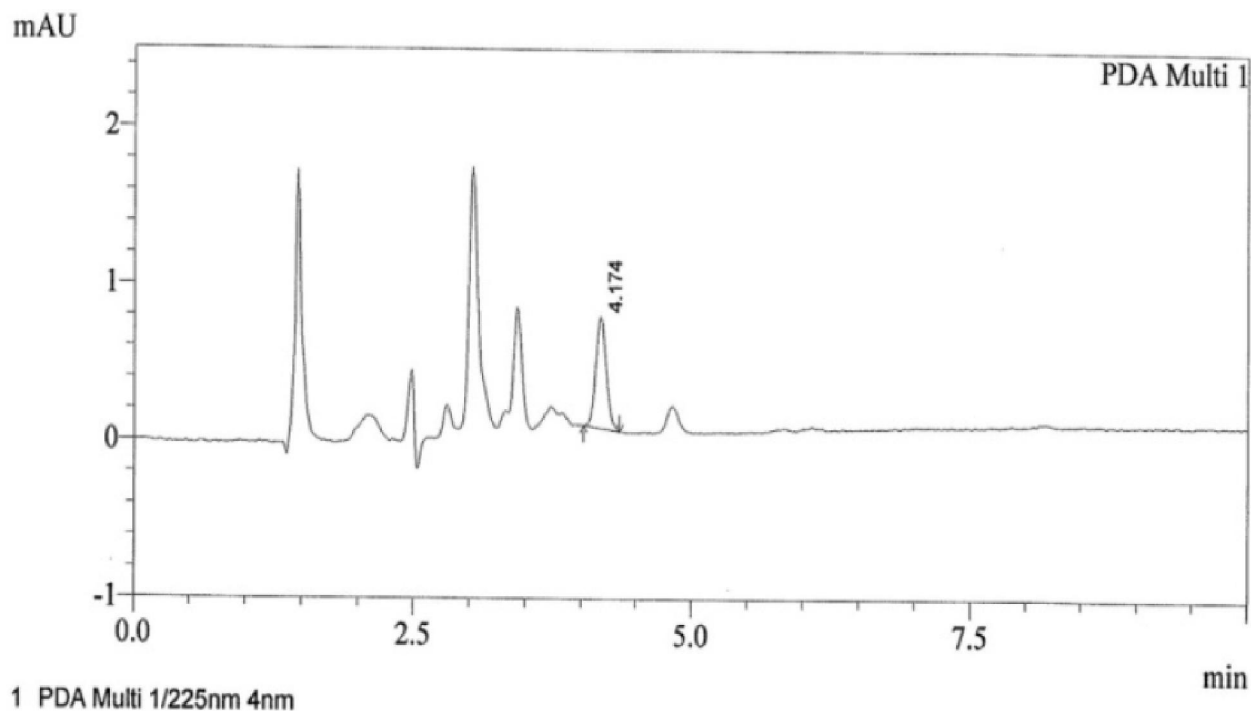
Temperature (°C)	Sample ID	Area	Slope Obtained from the calibration curve	Intercept Obtained from the calibration curve	*Dosing Level (g/kg)	Recovered Concentration (g/kg)	Purity corrected Concentration g/Kg	Recovery (%)
30	T2R1	1512061	30798.87	63.60	16.50	16.36	16.51	99.87
	T2R2	1510633	30798.87	63.60	16.50	16.35	16.49	99.78
	T2R3	1511248	30798.87	63.60	16.50	16.36	16.50	99.82

*Average of Three Replicates - 0th Days storage : 100% (16.50 g/kg); 7th Day after Storage : 99.82%; Standard Deviation : 0.047; Nitrogen Purge at 30°C

TABLE 4 : Temperature and flow rate data during vapour pressure determination of deltamethrin pure – definitive test

Days	Temperature (°C)		Average Flow Rate (ml/min)*					
	Oven 1	Oven 2	Oven 1			Oven 2		
			Te1R1	Te1R2	Te1R3	Te2R1	Te2R2	Te2R3
0	30	20	40	40	40	40	40	40
1	30	20	40	40	40	40	40	40
2	30	20	40	40	40	40	40	40
3	30	20	40	40	40	40	40	40
4	30	20	40	40	40	40	40	40
5	30	20	40	40	40	40	40	40
6	30	20	40	40	40	40	40	40
7	30	20	40	40	40	40	40	40
Average	30	20	40	40	40	40	40	40
	Total (V) m3		0.4032	0.4032	0.4032	0.4032	0.4032	0.4032

* Average flow rate of three measurements



1 PDA Multi 1/225nm 4nm

Figure 5 : Representative chromatogram of deltamethrin pure from the 30°C - definitive study

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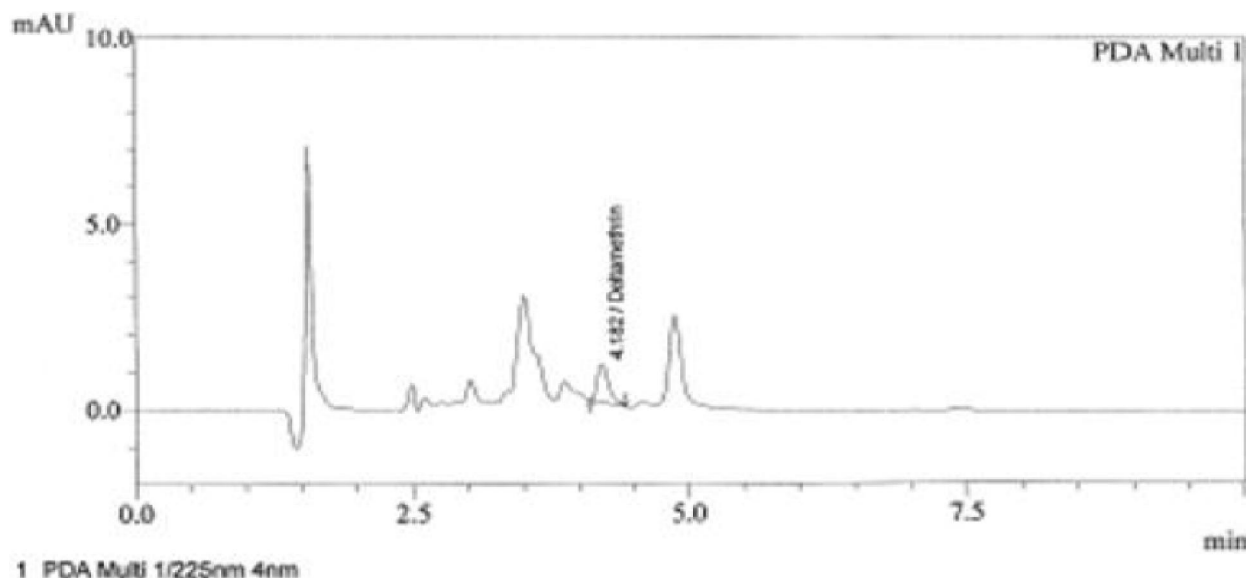


Figure 6 : Representative chromatogram of deltamethrin pure concentrate from the 20°C - definitive study

TABLE 5 : Determination of vapour pressure of deltamethrin technical at 30 °c

Sample ID	Area	Slope Obtained from the calibration curve	Intercept Obtained from the calibration curve	W (g)	V (m ³)	P (Pa) at 30 °C
Te1R1	5122	30798.87	63.60	1.66x10 ⁻⁶	0.4032	2.05x10 ⁻⁵
Te1R2	5086	30798.87	63.60	1.65x10 ⁻⁶	0.4032	2.04x10 ⁻⁵
Te1R3	5143	30798.87	63.60	1.66x10 ⁻⁶	0.4032	2.06x10 ⁻⁵
Average	5117	30798.87	63.60	1.66x10 ⁻⁶	0.4032	2.05x10 ⁻⁵
Standard Deviation						1.17x10 ⁻⁷

TABLE 6 : Determination of vapour pressure of deltamethrin technical at 20 °C

Sample ID	Area	Slope Obtained from the calibration curve	Intercept Obtained from the calibration curve	W (g)	V (m ³)	P (Pa) at 20 °C
Te2R1	4225	30798.87	63.60	1.36x10 ⁻⁶	0.4032	1.63x10 ⁻⁵
Te2R2	4199	30798.87	63.60	1.35x10 ⁻⁶	0.4032	1.62x10 ⁻⁵
Te2R3	4216	30798.87	63.60	1.36x10 ⁻⁶	0.4032	1.63x10 ⁻⁵
Average	4213	30798.87	63.60	1.36x10 ⁻⁶	0.4032	1.63x10 ⁻⁵
Standard Deviation						5.17 x 10 ⁻⁸

TABLE 7 : Stability of deltamethrin pure from the coated sand sample definitive study – 7th day

Temperature (°C)	Sample ID	Area	Slope Obtained from the calibration curve	Intercept Obtained from the calibration curve	*Dosing Level (g/kg)	Recovered concentration in g/Kg	Purity corrected Concentration g/Kg	Recovery (%)
20	T ₄ R1	1510115	30798.87	63.6	16.57	16.34	16.49	99.53
	T ₄ R2	1514064	30798.87	63.6	16.57	16.39	16.53	99.79
	T ₄ R3	1512662	30798.87	63.6	16.57	16.37	16.52	99.70

*Average of Three Replicates - 0th Day Storage : 100% (16.57 g/kg); 7th Day after Storage : 99.67%; Standard Deviation: 0.132; Nitrogen Purge at 20°C

TABLE 8 : Henry's constant

Temp (°C)	Water Solubility "S"	Absolute temp (in Kelvin = °C+273.15) "T"	Gas constant rate "R"	Mm/atm	Vapour pressure (in Torr) "P"	GMW	Henry's Constant (Pa.m ³ /mol)
20	0.01	293.15	82.08	760	1.220 x 10 ⁻⁷	505.2	2.967 x 10 ³
30	0.01	313.15	82.08	760	1.537 x 10 ⁻⁷	505.2	2.517 x 10 ³

Formula = Henry's constant = $C_{\text{water}} / C_{\text{air}} = S \times T \times 82.08 \times 760 / P \times \text{GMW} \times 10^6$.

TABLE 5 and TABLE 6. From the data, the average vapour pressure values of Deltamethrin Pure at 30°C was 2.05x10⁻⁵ Pa and 1.63x10⁻⁵ Pa at 20°C. The results presented in TABLE 7 clearly show that test item Deltamethrin Pure is stable during the 7 days storage period at temperature 20°C. The average recovery of triplicate analysis of 1 g of sample after 7 days of storage was 99.67%.

The Henry's law constant of the test item, Deltamethrin Pure, was determined to be 2.967x10³ Pa.m³/mol at 20°C and 2.517x10³ Pa.m³/mol at 30°C the results are presented in the TABLE 8.

CONCLUSION

The vapour pressure of the test item, Deltamethrin Pure, was determined to be 1.63x10⁻⁵ Pa at 20°C and 2.05x10⁻⁵ Pa at 30°C.

The Henry's law constant of the test item, Deltamethrin Pure, was determined to be 2.967x10³ Pa.m³/mol at 20°C and 2.517x10³ Pa.m³/mol at 30°C.

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